

POROUS CERAMIC OR METALLIC COATINGS AND ARTICLES

This invention relates to a method for preparing porous metallic and ceramic articles and/or coated substrates. Particularly, this invention relates to prosthetic devices having a porous ceramic or metallic coating on a substrate and to perforated ceramic or metallic articles useful in or as prosthetic devices.

The use of porous ceramics in prosthetic devices is well known. In U.S. Pat. No. 3,314,420, ceramic devices comprising a porous ceramic structure are prepared by placing calcium carbonate in the ceramic. At high temperatures, i.e., on firing, the calcium carbonate decomposes into calcium oxide and carbon dioxide. The evolution of carbon dioxide causes porosity in the structure. These porous structures can be filled with plastic resin such as epoxy. The surface porosity of the articles is reinstated by leaching a portion of the uncured resin through the use of solvents. After leaching, the remainder of the resin is cured.

Another reference to preparing ceramic prosthetic devices wherein porosity is included for tissue growth and is obtained by including in the ceramic material calcium carbonate which, on firing, causes pore formation because of the evolution of carbon dioxide is "Potential of Ceramic Materials as Permanently Implantable Skeletal Prostheses" *J. Biomed. Mater. Res.* Vol. 4, pp. 433-456 (1970). Producing porosity by means of calcium carbonate, i.e., carbon dioxide, generally results in a ceramic material wherein the surface and edges of the pores are of a jagged configuration. Sharp, jagged surfaces in a prosthetic device can cause the bone to be resorbed because the body attempts to relieve high stress concentrations at the jagged surface by destruction of the bone by the body.

Porous ceramic articles have also been prepared by mixing aluminum oxide powder, water, polyvinyl alcohol and hydrogen peroxide. The mixture was placed in frames and heated until it would support itself. Then the frames were removed. Porosity was obtained by the evolution of oxygen upon the decomposition of the hydrogen peroxide. When the structures were almost dry, they were sintered. ("Compression Strength of Porous Sintered Alumina and Zirconia", *Journal of the American Ceramic Society*, Vol. 36, No. 2, February, 1953, p. 65-68).

Preparation of porous ceramics by first producing a pyrolyzable porous form which is later filled with alumina slurry is also known. (German Offenlegungsschrift No. 2,242,907).

Ceramics have been applied to substrates in a number of ways including flame spraying, sintering and die pressing and/or compaction. In flame spraying a ceramic coated structure is formed by projecting a stream of highspeed ceramic particles in a plastic state against a solid substrate. When the particles strike the cold substrate, they tend to become flat and almost instantaneously cooled so that they adhere to the substrate. Thus, the ceramic coating is built up in a layered fashion on a substrate. If small particles are used, substantial porosity is difficult to obtain. With larger particles, porosity is obtained but adhesion is not good.

In the sintering process a slurry of ceramic powder, water wetting agent, carbon particles or some other material which is capable of being destroyed by heat is placed on a substrate. The coated substrate is heated to

high temperatures to burn out the pyrolyzable material, e.g., carbon particles. A porous coating is obtained by the destruction of the pyrolyzable material. However, such coatings generally have the afore-mentioned sharp edges and tend to be weak in bonding strength between the substrate and the coating.

A third method uses a ceramic powder containing a pyrolyzable material pressed onto a substrate. The coated substrate is fired at high temperatures to remove the pyrolyzable material. This method is expensive and can involve an extensive amount of machining to expose the porosity in the ceramic.

A method was sought whereby a porous coating of ceramic or metallic materials with pores having smooth edges and surfaces could be securely attached to a substrate for use in, for example, prosthetic devices, and a method was sought to prepare porous, strong ceramic or metallic articles which contained pores with smooth edges and surfaces.

A method for preparing coated substrates has been found which results in coatings with the aforementioned properties. It comprises:

(A) contacting a substrate selected from the class consisting of a ceramic substrate and metallic substrate with a composition to provide a coating of said composition on at least a portion of said substrate, said composition comprising:

(1) 25 to 80 percent by weight of a material selected from the class consisting of ceramic powder and powdered metal wherein the number average of the longest dimension of the particles of the material is from about 0.1 to about 300 microns;

(2) 2.0 to 12 percent by weight of a binder capable of adhering said material particles; and

(3) 18 to 73 percent by weight solvent, at least a portion of said solvent being capable of being rapidly volatilized under the conditions of step (B);

(B) rapidly volatilizing at least a portion of said solvent of said composition on said substrate and

(C) sintering said coated substrate to form a coated substrate with a porous coating.

The method for preparing a perforated article comprises:

(A) preparing a composition comprising:

(1) 25 to 80 percent by weight of a material selected from the class consisting of ceramic powder and powdered metal wherein the number average of the longest dimension of the particles of said material is from about 0.1 to about 300 microns;

(2) 2 to 12 percent by weight of a binder capable of adhering said material particles; and

(3) 18 to 73 percent by weight solvent, at least a portion of said solvent being capable of being rapidly volatilized under the conditions of step (B);

(B) rapidly volatilizing at least a portion of said solvent of said composition to form a porous unfired article; and

(C) sintering said article.

The first method above is particularly applicable to preparing prosthetic devices.

Before discussing the various steps of the method of the present invention, the composition which is applied to the substrate and which is utilized in preparing the perforated articles will be detailed. The composition comprises 25 to 80 percent, preferably 45 to 65 percent by weight ceramic powder or powdered metal having the number average of the longest dimension of the particles in the powder from about 0.1 to about 300